



Three are at least two major criteria in formulating a sealant composition. The sealant must possess some degree of slump resistance at high service temperatures. Additionally, the sealant should have a good working viscosity in melt so it can be easily coated on to various substrates, and/or the sealant should have a low solution viscosity in solutions containing a high amount ( $\geq 30$  wt. preferably  $\geq 40$  wt.) of solids.

Styrene-butadiene-styrene block copolymers are known to be useful for sealants because of their combination of strength and elastomeric properties. Hydrogenated versions of these polymers (SEBS) are especially useful because of their enhanced resilience to oxidation and chemical attack. These polymers give the compositions in which they are used excellent temperature resistance properties but they tend to be high in molecular weight and thus so high in viscosity that it is difficult to coat the sealants made with them.

This invention relates to sealant compositions for use as insulation against air and moisture, sound-deadening, and other functions in construction, automotive, and consumer applications. More particularly, this invention relates to such compositions containing new high vinyl content hydrogenated vinyl aromatic hydrocarbon-butadiene-vinyl aromatic hydrocarbon (SEBS) block copolymers.

This invention provides sealant compositions which comprises a hydrogenated vinyl aromatic hydrocarbon-butadiene-vinyl aromatic hydrocarbon (SEBS) block copolymer which has an overall weight average molecular weight of from 30,000 to 300,000, a vinyl aromatic hydrocarbon block copolymer which has an overall weight average molecular weight of at least 45% by weight (%wt), preferably 45 to 90%, and a sealant composition-promoting resins such as tackifying resins. For every 100 parts by weight of block copolymer, there should be 20-400, and preferably 60 to 350 parts by weight of adhesive-promoting resins. Optionally, the sealant composition may further comprise polyvinyl alcohol, and/or solvents.

The preferred structure for the block copolymers used herein is linear, i.e., S-E-B-S. However, block copolymers having branched, radial, and star structures may also be useful in this invention. Such structures may be generically represented by the formula

$$(A-B)^x-y$$

Quite aside from sealant compositions in terms of high temperature properties must be accepted. The large syrene endblocks in the higher molecular weight SBS polymers are resistant to flow but give excellent high service temperature performance. Examples of composites solutions are the use of a lower molecular weight polymer and blending in a relatively low molecular diblock polymer of this type. Thus it can be seen that it would be advantageous to make an easily coatable sealant composition and retain or enhance the high temperature properties achievable with the higher molecular weight SBS polymers.

Anionic polymerization of conjugated diene hydrocarbons with lithium initiators is well known as described in U.S. Patents Nos. 4,039,593 and RE. 27,145 which describes incorporation of conjugated diene polymers into each lithium menes with a monolithium, dilithium, or polylithium initiator which builds a living polymer backbone at each lithium site. Typical living polymer structures containing polymerized conjugated diene hydrocarbons are:

The hydrogenation of these polymers may be carried out by a variety of well established processes including hydrogenation of such catalysts as Raney Nickel, noble metals such as platinum, and palladium and soluble transition metal catalysts. Suitable hydrogenation processes which can be used are ones wherein the diene-containing polymer or copolymer is dissolved in an inert hydrocarbon diluent such as cyclohexane and hydrogenated by reaction with hydrogen in the presence of a soluble hydrogenation catalyst. Such processes are disclosed in U.S. Patent Nos. 3,113,986, 4,226,952 and Reissue 27,145, the disclosures of which are herein incorporated by reference.

wherein R is an aliphatic, cycloaliphatic, alkyl-substituted cycloaliphatic, aromatic or alkyl-substituted aromatic hydrocarbon radicals having from 1 to 20 carbon atoms.

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The anionic polymerization of the conjugated diene hydrocarbons is typically controlled with structure modifiers such as diethyl ether or ethyl glyme (1,2-dieethoxyethane) to obtain the desired amount of 1,2-addition. As described in Figure 27 145 which is incorporated by reference herein, the level of 1,2-addition of a butadiene polymer or copolymer can greatly affect the isotropic properties after hydrogengation. The 1,2-addition of butadiene polymers significantly and surprisingly additionally influences the polymer as described above. A 1,2-addition of about 40% is achieved during polymerization at 50°C with about 6% by volume of diethyl ether or about 200 ppm of ethyl glyme in the final solution. A 1,2-addition of about 47% (within the scope of this invention) is achieved during polymerization by the presence of 250 ppm of ortho-dimethoxybenzene (ODMB) in the final solution. A 1,2-addition of about 78% (within the scope of this invention) is achieved during polymerization by the presence of about 300 ppm of 1,2-dieethoxypropane (DEP) in the final solution.

wherein B represents polymersized units of one or more conjugated diene hydrocarbons such as butadiene or isoprene, A represents polymerized units of one or more vinyl aromatic hydrocarbon compounds such as styrene, X is the residue of a monoaluminum initiator such as sec-butyllithium, and Y is the residue of a dilithium initiator such as the diadduct of sec-butyllithium and diisopropenylbenzene. Some structures, including those pertaining to polythium initiators or analogs, units of structure and a conjugated diene, generally have limited practical utility although known in the art.

Li-A-B-Y-B-A-Li

U-B-Y-B-U

X-A-B-A-LI

X-A-B-L

EP 0 863 193 A1

A composition of the instant invention may further contain plasticizers, such as rubber extender plasticizers, or 6204 oil made by Arco and napthenic process oils, e.g. Shellflex® 371 oil made by Shell. The amounts of plasticizer high saturates content oils and napthenic oils. Preferred plasticizers are highly saturated oils, e.g. Tufflo® 6056 and compounds containing oils of organic or inorganic pigments and dyes. Plasticizers are well-known in the art and include both A large part, dependent upon the specific polymer employed in the respective sealant composition.

may be used as well as combinations of solid and liquid resins. The selection of the particular tackifying agent is, in large part, determined by the properties of the polymer employed in the respective sealant composition. The may be used as well as combinations of solid and liquid resins, i.e., softening points of solid resins less than room temperature, preferably 80 to 115°C, as determined by ASTM E28. Liquid resins, i.e., softening points of solid resins may be from 40°C to 140°C, such as Fegalrez® resin made by Hercules. Ring and ball softening point of polyisobutylene resin may be from 40°C to 140°C, such as Escorze® 5000 series resin made by Exxon or a hydrogenated polyisobutylene resin of cyclopentadiene resin color stability, it is preferred that the tackifying resin be a saturated resin, e.g., a hydrogenated cyclopentadiene resin and liquid resins. An example of a liquid resin is Adbac® LV resin from Hercules. To obtain good thermooxidative and resins, esters of rosins, polyterpenes, terpenophenol resins and polymerized mixed olefins, lower softening point resins and liquid resins. Another adhesion promoting resins which are also useful in the compositions of this invention include hydrogenated

Other adhesion promoting resins which are also useful in the compositions of this invention include hydrogenated copolymers 20-80 weight percent of piperylene and 80-20 weight percent of 2-methyl-2-butene.

comprises 20-80 weight percent of piperylene and 80-20 weight percent of 2-methyl-2-butene. Other tackifying resins may be employed wherein the resins copolymer dimer, as taught in U.S. Patent No. 3,577,398. Other tackifying resins may be employed wherein the resins copolymer point of about 95°C. This resin is available commercially under the trade name Wingtack® 95 and is prepared by the cationic polymerization of 60% piprene, 10% isoprene, 5% cyclo-pentadiene, 15% 2-methyl-2-butene and about 10% application.

A common tackifying resin is a diene-olefin copolymer of piperylene and 2-methyl-2-butene having a softening per 100 parts polymer can be used or the sealant will not have the visco-elastic properties required to resist flow after the low viscosity and economies required for sealant applications. No more than 400 pbw adhesion promoting resin is compatible with the polymer, generally from 20 to 400 parts per hundred parts of polymer by weight (pbw), preferably 60 to 350 pbw. For every 100 parts by weight (pbw) of copolymer, there should be at least 20 pbw of resin to achieve 15 to 35 %wt.

The poly(vinyl aromatic hydrocarbon) content, typically the polystyrene content, is preferably in the range from 15 block weight average molecular weight is preferably 5,000 to 32,000.

preferably has an overall weight average molecular weight of from 45,000 to 200,000. The vinyl aromatic hydrocarbon

1. Modern Size-Exclusion Liquid Chromatography, W. W. Yau, J. J. Kirkland, D. D. Bly, John Wiley & Sons, New York, NY, 1979.

2. Light Scattering from Polymer Solution, M. B. Huglin, ed., Academic Press, New York, NY, 1972.

3. W. Kaye and A. J. Hawlik, *Applied Optics*, 12, 541 (1973).

4. M. L. McConnell, American Laboratory, 63, May, 1978.

and in the same solvent used for the light scattering. The following references relate to the subject of measuring molecular weight.

The light scattering measurements are performed as a function of scattering angle and of polymer concentration using standard procedures. The differential refractive index (DRI) of the sample is measured at the same wavelength as dissolved in a suitable solvent at a concentration less than 1.0 gram of sample per 100 milliliters of solvent and a radial or star polymer is to measure the weight average molecular weight by light scattering techniques. The time of arrival at a UV of refractive index detector is not a good indicator of the calibration, and, hence, the time the packed GPC columns in the same manner as do the star shaped molecules do not separate and elute throughout as easy to make using GPC. This is because the final coupled radial or star polymer is not as straightforward as benzene gels. The solvent is tetrahydrofuran and the detector is a refractive index detector.

Measurements of the true molecular weight of the final coupled radial or star polymer is to use for the peak value is between the number and the weight average molecular weight is the molecular weight of the main species shown on the chromatograph. For polydisperse polymers the weight average molecular weight should be calculated from the chromatograph. The peak molecular weight is the molecular weight of the molecules described to report the "peak" molecular weight of the narrow molecular distribution observed. Usually, the molecular weight number average molecular weight ratio approaches unity, and it is both convenient and adequate to describe the arms of star polymers before coupling are ratio approaches unity).

etc., or the arms of star polymers or unassembled linear segments of polymers such as mono-, di-, triblock, (GPC), where the GPC system has been appropriately calibrated, typically with polystyrene standards of known molecular weight. For anionically polymerized linear polymers, the polymer is essentially monodisperse (weight average molecular weight). For anionically polymerized linear polymers, the polymer is essentially monodisperse (weight average molecular weight ratio approaches unity), and it is both convenient and adequate to describe the arms of star polymers before coupling are ratio approaches unity).

The molecular weights of linear polymers or unassembled linear segments of polymers such as mono-, di-, triblock,

fillers for constructions which will be baked (for example, in a paint baking oven) after the sealant is applied. This would sealant compositions of this invention can be used for many applications. Particularly preferred is their use as gap fillers for constructions which will be baked (for example, in a paint baking oven) after the sealant is applied. This would

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sealant compositions may then be used in a wide variety of applications. Alternatively, the ingredients may be blended into a solvent.

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The resultant compositions of blending are known to the art and any method that produces a homogeneous blend is satisfactory. Various methods of blending are known to the art and any method that produces a homogeneous blend is satisfactory. Preferredly between 50°C and 200°C, until a homogeneous blend is obtained, usually less than three (3) hours. The sealant compositions of the present invention can be prepared by blending the components at an elevated temperature, preferably between 50°C and 200°C, until a homogeneous blend is obtained, usually less than three (3) hours.

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The sealant compositions of the present invention can be prepared by blending the components at an elevated

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having properties suitable for many applications.

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A formulator skilled in the art will see tremendous versatility in the polymers of this invention to prepare sealants

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containing is as low as possible to minimize shrinkage.

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pigment will be selected to give appropriate durability and color. Since sealants are applied in fairly thick layers, solvent

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usually used. Resins and plasticizers will be selected to maintain low modulus and minimize dirt pick-up. Fillers and

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of whitishaniding this movement. Since sealants are frequently exposed to the weather, the hydrogenerated polymers are

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Since the two substrates frequently move relative to each other, sealants are usually low modulus compositions capable

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Sealants are gap fillers. Therefore, they are used in fairly thick layers to fill the space between two substrates.

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Sealants are gap fillers. Thereafter, they are used in fairly thick layers to fill the space between two substrates.

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action of properties needed in the composition for any specific adhesive, coating or sealant application.

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All sealant compositions based on the polymers of this invention will contain some combination of the various

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taught herein.

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All sealant should be compatible with the essential stabilizers mentioned hereinabove and their intended function as

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stabilizers should be compatible against, for example, ozone, ultra-violet radiation. However, these additional

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durig the life of the article against, for example, oxygen, ozone, ozone and ultra-violet radiation. These may be for protection

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Additional stabilizers known in the art may also be incorporated into the composition. These may be for protection

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(unroyal), organoxo@ 1010 with bis(2,4-di-t-butyl)penataerythritol diphenosphate (Uniranoxy@ 626 from Borg-Warmer).

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Unphenylpropionate-methane (organoxo@ 1010 from Ciba-Geigy) with triis(nonylphenyl)-phosphate (Polygard@ HR from

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phenolics with aryl phosphites, such as hydroxyphenylpropionates with aryl phosphites or thioethers, or amino

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phenolics with phosphites or thioethers, such as hydroxyphenylpropionates with aryl phosphites or thioethers, or hindered

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Combination of primary and secondary antioxidants are preferred. Such combinations include sterically hindered

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Typically, at least one antioxidant is present as stabilizer.

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The sealant formulation, preferably 0.5 to 10 % by weight, based on the solvent-free portion of

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Stabilizers are typically present in a total amount from 0.1 to 10 % by weight, based on the solvent-free portion of

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the composition.

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the composition.

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Skin formation and color formation are stabilizers which inhibit or retard heat degradation, oxidation,

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Optional components of the present invention are stabilizers which inhibit or retard heat degradation, oxidation,

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the solvent blend, preferably between 10 and 70 %, such as e.g. 50 % w/w.

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of the particular polymer used in the formulation. Usually, the amount of polar solvent used is between 0 and 80 % w/w in

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isopropyl alcohol. The amount of polar solvent chosen and on the structure

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esters such as isopropyl acetate and n-butyl acetate, ketones such as methyl isobutyl ketone, and alcohols such as

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a solvent blend consisting of a hydrocarbon solvent such as hexane, naptha or mineral spirits may also be used. If desired,

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are suitable. Aliphatic hydrocarbon solvents such as toluene, xylene, or Shell Cyclo Sol 53 (trade mark)

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solvent or blend of solvents. Aromatic hydrocarbon solvents such as toluene, xylene, or Shell Cyclo Sol 53 (trade mark)

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if the sealant will be applied from solution, the organic portion of the formulation will be dissolved in a

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sealant formulation. An especially preferred filter is titanium dioxide.

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sealant formulation. An especially preferred filter is titanium dioxide.

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If filter is present, the amount of filter is typically at least 10 % w/w based on the solvent free portion of the

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solvent free portion of the formulation depending on the type of filter used and the application for which the sealant is

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talc, silica, zinc oxide, and titanium dioxide. The amount of filter usually is in the range of 0 to 65 % w/w based on the

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sealant such as its weatherability. A wide variety of filters can be used. Suitable filters include calcium carbonate, clays,

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toluene-alpha methylestyrene copolymers and polystyrene resins.

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Toluene point is in the range 80-115°. Useful resins include cumarone-indene resins, polystyrene resins, vinyl

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or aromatic resins having higher and lower softening points may also be used. In that case typically the average soft-

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ing formulation. Normally, these resins have ring and ball softening points between 80°C and 115°C although mixtures

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resins may be employed as reinforcing resins, provided that they are compatible with the particular polymer used in

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the sealant formulation may further contain poly(vinyl aromatic hydrocarbon) block reinforcing resins. Aromatic

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resins may be reinforced as reinforcing resins, provided that they are compatible with the particular polymer used in

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the sealant formulation may vary from 0 to 150 phr, preferably at least 5 phr, preferably at least 10 phr.

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employed in the invention composition may vary from 0 to 100 phr, and most preferably between

Temperature dependent properties, such as shear adhesion failure temperature (SAFT) and slump temperature, were measured. A Brookfield Viscometer model RVT-D and spindle 29 was used to measure the viscosity at 117°C. To measure the slump temperature, the sealant formulation was poured hot and allowed to solidify in metal channels with the following dimensions: 2.5cm wide, by 2.5cm high, and 1.25cm deep. The channels were placed vertically in an oven and the temperature was raised in 5°C increments, allowing the sample to equilibrate for 30 minutes at each temperature before increasing the temperature again. The slump temperature was determined at which the sample sagged more than 3/16 inch in the channel. SAFT was determined on a lap-shear bond of 2.5cm x 2.5cm area on an aluminum surface under a load of 190g. The temperature was ramped up from 40°C in 5°C increments every 10 minutes until bond failure occurred.

## Table

Sealant Results				
Polymer	Sealant Viscosity at 177° (350°F) (CP)	Shear Adhesion Failure Temperature (°C)	Silmp Temperature (°C)	A
B	33,500	73	105	
PP-5828	1,190	54.5	80	
PP-5819	5,280	54.1	80	
PP-5823	1,800	52.6	60	
	400	48.1	55	

Table 1

Polymer Descriptions				
Polymer	MW (real)	SEBS Block Description	1,2 Bd level	PSG
A	67,000	10-47-10	38%	29.9%
B	56,000	10-39-10	78%	29.6%
PP-5328	56,000	10-39-10	78%	29.6%
B	50,000	7.5-35-7.5	38%	30%
PP-5319	38,000	6-26-6	47%	29.5%
PP-5323	35,000	6-23-6	78%	29.3%

PP5823 is an SEBS block copolymer with a high vinyl content. Its molecular characteristics are compared with those of Polymer A, a commercial polymer whose viscosity is considered too high for most, if not all, commercial sealant applications. It can be seen that PP5828 and Polymer A are very similar except for the vinyl content: 78% of the rubber block of PP5828 is in a 1,2-microstructure compared to 38% for Polymer A. The flow properties of PP5828 are dramatically better than Polymer A as indicated by sealant viscosity (more than an order of magnitude lower). Polymer B is the block copolymer of this type that is currently used to make sealant formulations commercially. The sealant viscosity of this formulation, made with PP5828, is one fifth of that of the formulation made with Polymer B while the SFT and slump temperature are the same. Similarity, PP5823 (78% 1,2-addition) exhibits much lower sealant viscosity than either Polymer A or B. PP5819 has an intermediate level of 1,2-addition (47%). but is still markedly better (lower) in sealant viscosity than Polymers A or B. The low sealant viscosity measured in sealant composition can be mixed, pumped, and applied more easily than sealants with higher viscosity.

### Example 1

Include their use in automobile manufacture and in appliance manufacture. Another preferred application is their use in gasketing materials, for example, in lids for food and beverage containers. The unhydrogenated *pr* curors may also be used in these applications.

Variations of sealant compositions that are subjects of this invention will include adhesives, such as contact and structural adhesives, mastics, diaper assembly and personal care adhesives, and laminating adhesives. Especially useful will be the low viscosity characteristic of high vinyl ethylene/butylene rubber blocks for ease of adhesive application. e.g., sprayability.

composition as claimed in any one of the preceding claims.

8. Sealant solutions containing a solvent and at least 30 % by weight on the basis of the total solution of a sealant

7. Sealant composition according to any one of the preceding claims, further comprising a reinforcing resin.

6. Sealant composition according to any one of the preceding claims, further comprising a plasticizer.

5. Sealant composition according to any one of the preceding claims further comprising a filler.

4. Sealant composition according to any one of claims 1-3 wherein the vinyl aromatic hydrocarbon block molecular weight is from 5,000 to 32,000.

3. Sealant composition according to claim 1 or 2 wherein the overall weight average molecular weight is from 45,000 to 200,000.

2. Sealant composition according to claim 1 wherein the vinyl content is from 45 to 90% by weight.

(a) 100 parts by weight of a hydrogenated vinyl aromatic hydrocarbon butadiene-vinyl aromatic hydrocarbon block copolymer which has an overall weight average molecular weight of from 30,000 to 300,000, a vinyl aromatic hydrocarbon block weight of at least 45% by weight, and diene block has a vinyl content of at least 45% by weight; and (b) 20-400 parts by weight of an adhesion promoting resin.

1. Sealant composition which comprises:

## Claims

Ondina 68 is a hydrogenated paraffinic processing oil (plasticiser)  
Krisallex F100 is an aromatic reinforcing resin  
Regalite R101 is a hydrogenated hydrocarbon tackifying resin

Sealant formulation		Table 3	
A	PP 5828	Regalite R 101	Ondina 68
1	160 g	44.0 g	10.4 g
		9.6 g	9.6 g
		16.0 g	16.0 g
		-	-
		n-butyl acetate	80.0 g
		10.4 g	10.4 g
		80.0 g	80.0 g
		toluene	40.0 g

Block copolymers PP 5828 and B described in Example 1 were used to prepare sealant formulation solutions containing 40 % by weight of solids as shown in Table 3. The solution viscosity was determined at 25°C using a Brookfield viscometer. The sealant formulation containing polymer B (not according to the invention) had a solution viscosity of 89.2 centipoise, whereas the sealant formulation containing polymer PP 5828 according to the invention had a solution viscosity of 22.8 centipoise. A low solution viscosity at 40 % solids content is advantageous as the sealant can then be easily applied, or alternatively, the solids content can then be increased to e.g. 50-90 % by weight, preferably 65 to 85% by weight.

## Example 2

DOCUMENTS CONSIDERED TO BE RELEVANT											
Category	Citation of document with indication, where appropriate. of relevant passages	Relevant to claim	CLASSIFICATION (incl.6) APPLICATON OF THE CATEGORI								
A	WO 95 12645 A (SHELL INT RESEARCH) 11 May 1995 * page 10, line 26 - page 14, line 16 *	1-8 C09K3/10 C08L53/02	US 4 242 245 A (ALLISON GEORGE M III) 30 December 1980 * the whole document *								
A	EP 0 322 055 A (SHELL INT RESEARCH) 28 June 1989 * the whole document *	1-8 C09K3/10 C08L53/02	FR 2 423 460 A (BOSTIK SA) 16 November 1979 * page 5, line 11 - page 9, line 18 *								
A	EP 0 367 165 A (HERCULES INC) 9 May 1990 * claims *	1-8 C09K3/10 C08L53/02	EP 0 822 227 A (SHELL INT RESEARCH) 4 February 1998 * the whole document *								
P,A	EP 0 822 227 A (SHELL INT RESEARCH) 4 February 1998 * claims; table I *	1 C09K3/10 C08L53/02	The present search report has been drawn up for all claims								
<table border="1"> <tr> <td colspan="2">CATEGORY OF CITED DOCUMENTS</td> </tr> <tr> <td colspan="2">T : inventor or promoter nationality indicating the invention X : partnership between it's inventors E : earlier patent document published on, or D : document cited in the application Y : partnership between it's inventors A : document cited for other reasons O : non-written disclosure P : transnational disclosure F : transnational disclosure G : member of the same family, corresponding document</td> </tr> </table>				CATEGORY OF CITED DOCUMENTS		T : inventor or promoter nationality indicating the invention X : partnership between it's inventors E : earlier patent document published on, or D : document cited in the application Y : partnership between it's inventors A : document cited for other reasons O : non-written disclosure P : transnational disclosure F : transnational disclosure G : member of the same family, corresponding document					
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<table border="1"> <tr> <td>THE HAGUE</td> <td>11 June 1998</td> <td>Putz, C</td> <td></td> </tr> <tr> <td>Place of search</td> <td>Date of completion of the search</td> <td>Examiner</td> <td></td> </tr> </table>				THE HAGUE	11 June 1998	Putz, C		Place of search	Date of completion of the search	Examiner	
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